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A Study of Eutectics of Certain Fused Salts

William D. Trethewey

A STUDY OF THE EUTECTICS OF CERTAIN FUSED SALTS

A Thesis

Submitted To The Department of Metallurgy

In Partial Fulfillment of the Requirements For

The Degree of Bachelor of Science in

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Introduction

Considerable work has been done investigating the freezing point curves of fused salts by Carlo Sandonnini, Mario Amadori, and Umberto Sborgi [1]. but little has been written describing the appearance of their eutectic structures when observed under the microscope. In the preparation of this thesis, the writer used the equilibrium diagrams as determined by these men as far as possible in order to determine the most probable directions in which to proceed. However, several combinations of salts were investigated for which the freezing point curves were not known. In these cases, the composition of the eutectic mixture was approximated. Shortness of time and inadequateness of equipment limited the investigation to only a few salts.

Eutectics

If the components of a binary liquid mixture are immiscible in the solid state, the freezing point curve is discontinuous. (Rooseboom's Type V). In the simplest case it consists of two descending branches which intersect at that point which has the lowest freezing temperature of the mixture. This point is known as the eutectic temperature and the composition of the salts is known as the eutectic mixture. The eutectic mixture is further distinguished by the fact that the two components crystallize out simultaneously in the proportions in which they were present in the liquid. The work "eutectic" is derived from the Greek εὖ, easily, and τήκω, I melt. Hence, eutectic means "that which is easily melted." The word εὔτηκτος was used by Aristotle in the sense of easily soluble or digestible.

Mixtures which contain an excess of A in comparison with the eutectic mixture deposit A on freezing; mixtures which contain an excess of B deposit B crystals on freezing. This freezing of primary crystals alters the composition of the residual liquid and the freezing point falls continuously until the eutectic composition is reached. The solidification of the remaining liquid is then completed at constant temperature. (See Figure 1.)

At the eutectic point, the mixture is saturated with <u>both</u> components and must therefore precipitate both kinds of crystal of A and one of B at various points in the remaining liquid, as fast as the heat set free by crystallization can be carried away,

until solidification is complete, the temperature and the composition of all three phases (melt, A crystals, and B crystals) remaining constant and unchanged during the process. At any locality in the melt where an A crystal is precipitated the surrounding liquid is saturated in B material and a B crystal precipitates next to the A. This dissociation of the eutectic liquid into crystals of A and B is known as the eutectic reaction.

The microstructure of the fusion is simple to predict. It will show crystals of A which have come out in the earlier stages of freezing, proir to reaching the eutectic point, and grown to considerable size, so-called primary crystals of A, surrounded by alternate, smaller, crystals (since each has had less time to grow) of A and B in a finely divided eutectic matrix or background, (shown diagramatically second from the felt in the bottom row of structures, in Figure 1.). The primary A crystals might resemble the pebbles in concrete. Both the large and the small A crystallites as well as the small B crystallities will be pure in accordance with our assumption of complete insolubility in the solid state. A structure containing two crystalline varieties as this one does is called a "duplex" structure. Thus we see how a reading of the diagram of Figure 1. enables one to predict the structure of any given mixture of salts, both during its cooling and after it has reached room temperature.

The appearance of these two mixtures x and y at successive stages during cooling of each is shown at the left and right

of Figure 1. At the bottom of the diagram are shown the structures of several other mixtures between pure A and B, when slowly cooled to room temperature. It will be noticed that the proportion of primary A crystallites increases from zero at the eutectic composition toward 100 per cent at the pure A ordinate, while that of primary B increases from zero for the eutectic toward 100 per cent for a mixture of pure B.

The proportion of eutectic present is, of course, 100 per cent for a mixture of composition c; 0 per cent for pure A or pure B and inversely proportional as the distance between f and c, and between c and g.

The eutectic mixture sometimes formes definite pattern. If the eutectic consists of alternate bonds of the two components; it is called a lamellar eutectic. If one component forms globules embedded in a matrix of the other, the eutectic is known as a globular eutectic. If one component appears like small polyhedral crystals arranged in a matrix of the other, it is designated as a polygonal eutectic.

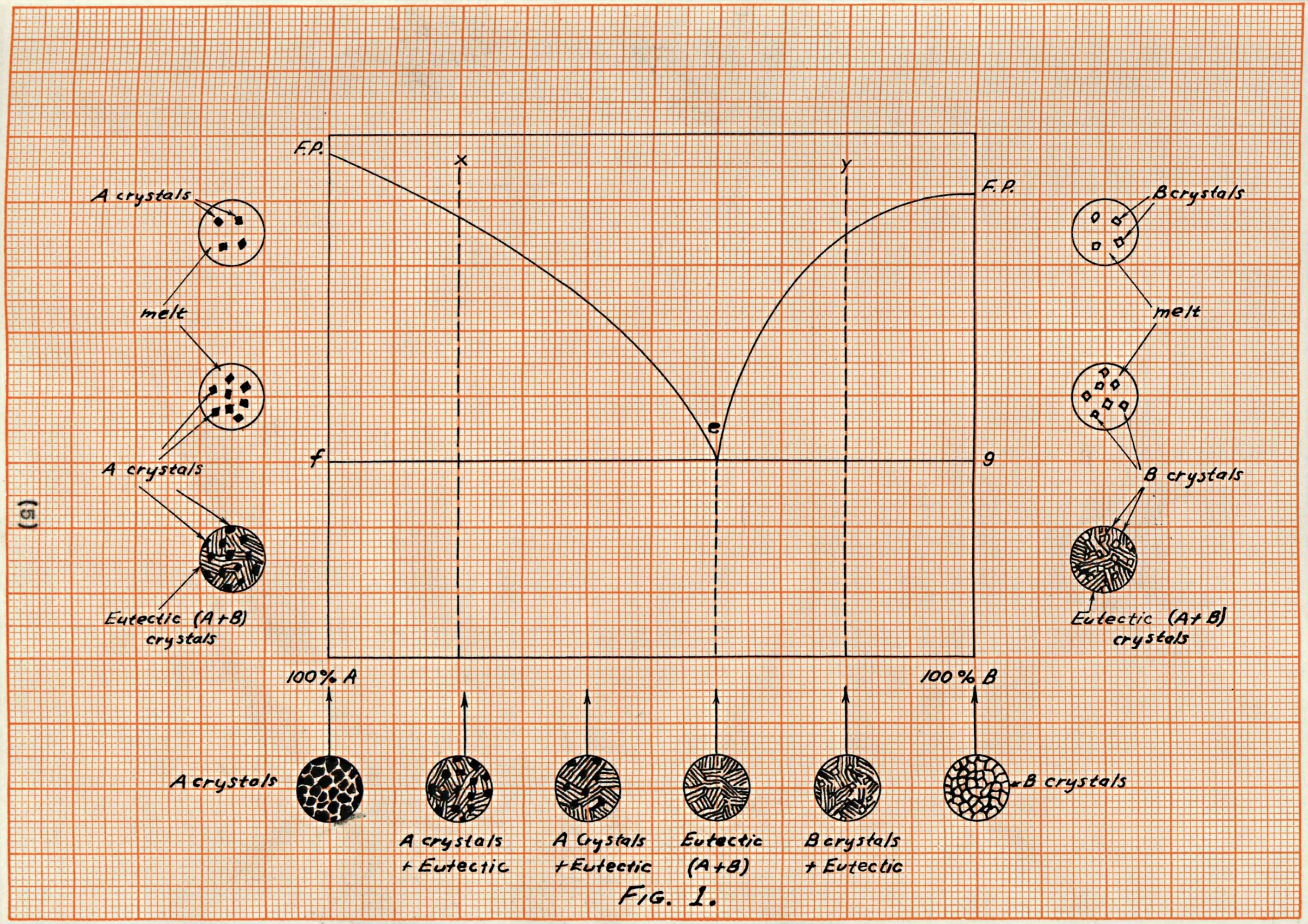

F.P.
X
Y
F.P.
A crystals
melt
A crystals
Eutectic (A+B) crystals
e
f
g
B crystals
melt
B crystals
Eutectic (A+B) crystals
100% A
100% B
A crystals
A crystals + Eutectic
A Crystals + Eutectic
Eutectic (A+B)
B crystals + Eutectic
B crystals

FIG. 1.

Experimental Procedure

The experimental procedure consisted of fusing mixtures of two salts containing one common ion but dissimilar in color, preparing the fusions for examination, and describing the appearance of these fusions under the microscope by means of sketches, photographs, and written discussions.

If the equilibrium diagram of the two salts was known, they were ground together in small mortar in such proportions that the resulting fusion would consist principally of eutectic crystals. If the equilibrium diagram was not known, several different proportions were mixed in attempting to discover an eutectic mixture.

After grinding the mixture, it was melted in a small glazed crucible over a Bunsen burner. Since it is impossible to heat the contents of even a small crucible above 1000°C with such a burner, and moreover, since it is unlikely that temperatures even approaching this were attained, the investigation was limited to salts of comparatively low melting points.

After the fusion was complete, the burner was withdrawn from beneath the crucible, and the cooling was allowed to proceed as rapidly as convection would permit. Exceptions to this method were observed when piping seemed to be characteristic of the fusion.

After the crucible had cooled to such a temperature that it could be handled with the fingers, the fusion was tapped out and marked with a small gummed label.

Preparation of Specimens for Microscopic Examination: Little can be learned by the microscopic examination unless the surface to be examined is properly prepared. Improper preparation is likely to remove all important inclusions, erode crystal boundaries, or fuse one crystal into another, ultimately producing a microstructure that is entirely different from that of the originals cooled fusion. An examination of a poorly prepared specimen would lead to incorrect interpretations and unreliable conclusions.

In general, the writer's procedure of specimen preparation consisted of first obtaining a flat surface by means of a file, followed by a smoothing operation by means of grinding on a series of emery papers of decreasing grit size, and lastly lightly rubbing the surface with a cloth slightly moistened with water.

After the fusion had been removed from the crucible, its bottom was ground down by means of a fine file to erace the concavity produced by the crucible. This operation was done carefully in order to aviod removing crystals loosely included in the matrix.

The first grinding paper was a No. O French emery paper. The emery paper was placed on a clean sheet of flat glass and the specimen was gently drawn back and forth across the entire length of the paper, under a moderately applied aressure. The fused salts were usually so soft that care had to be taken that a very light pressure was used, in order to prevent the introduction of deepseated scratches.

While being ground on the first emery paper, the fusion was held so that the new scratches which were introduced were approximately at right angles to the old scratches on the surface, resulting from the previous flattening operation. The completion of grinding on one particular paper was recognized by the disappearance of the old scratches and their replacement by newer, finer scratches.

The subsequent grinding operation were the same as described. Two additional emery papers were used--No.000 and No. 00 French papers.

The preparation of the specimen was completed by lightly rubbing the surface with a cloth slightly moistened with water.

Ethyl alcohol which commonly contains about 2% of water was experimentally used as an etchant but without appreciably success In all specimens the structures were so apparent as to render etching unnecessary.

Etchants which would produce different colors on different constituents of the structure (such as thin oxide coating or reaction products) thus effecting a contrast and distinction between them, were not tried but subsequent investigators might find them helpful.

Photomicrographs

The photomicrographs were made on a table microscope equipped with a special attachment and a small Leica camera. Better results undoubtedly could be obtained with a micrometallograph, but this was not available at the time the photographs were taken. The microscope was fitted with a 16 mm. objective and a 10x ocular giving an approximate magnification of 100. The film used was Kodak Panchromatic Super X and the time of exposure varied from two to five minutes depending upon the color of the specimen. Oblique lighting was found to illuminate the object better than indirect lighting. This oblique illumination caused the structure to stand out in striking relief, due to the shadows cast. A B-58 (green) filter was used.

The film was immersed in Kodak Dk-20 developing solution for fifteen minutes and then washed. After washing, the film was "fixed" in Kodak F-5 solution for fifteen minutes, again washed for thirty minutes, and then dried. The positives were printed on a glassy finish bromide paper.

Although the photographs appear to be out of focus, this is not the case. The microscopic appearance was very simular to this and great care was taken in focusing. Even the use of objectives of greater numerical aperature did not seem to improve this appearance.

All specimens were mounted in plasticene in such a way that the surface of the specimen was in a plane perpendicular to the optical axis of the microscope. Because of a lack of time, no

specimens were mounted in pressure-molding plastics such as bakelite or Lucite, but their use was planned and is suggested, especially for friable fusions which would not stand the usual preparation of filing and grinding.

RESULTS

1. $CuCl_2$- KCl. Lamellar eutectic, discontinuous brown $CuCl_2$ in white KCl. Figure 2-a. Eutectic at approximately 70% $CuCl_2$.

2. $CuCl_2$-NaCl. Same as 1 except eutectic appeared as small globules of $CuCl_2$ in a matrix of NaCl (rosettes). Eutectic at about 70% $CuCl_2$. Figure 2-b.

3. $CdCl_2$-$FeCl_3$. When first heated, water of crystallization boiled. After the water was driven off, the mixture was difficult to fuse. The mixture was removed from the crucible, reground, and reheated without successful fusion.

4. $CoCl_2$-$FeCl_3$. Same as 3.

5. $NiCl_2$-KCl. Fused easily. No apparent eutectic structure.

6. $CuCl_2$-$NiCl_2$. Mixture sintered without fusing.

7. $CdCl_2$-$NiCl_2$. Same as 6.

8. $CuCl_2$-$PbCl_2$. Good lamellar eutectic structure. Figure 2-e.

9. $CuSO_4$-Na_2SO_4. Would not stand filing and grinding.

10. $CoSO_4$-Na_2SO_4. Same as 9.

11. $CuCl_2$-$ZnCl_2$. Zinc chloride deliquesced so rapidly as to render examination impractical.

12. $CuCl_2$-$BaCl_2$. Fusion too weak to stand filing and polishing.

13. $CuSO_4$-$CoSO_4$. Infusible.

14. $K_2Cr_2O_7$-KNO_3. Long acicular red crystals in yellow matrix. Polyhedral eutectic structure.

15. $FeCl_3$-NaCl. Black and white crystals. No eutectic.

16. $CuCl_2$-$CdCl_2$. Long dark-blue crystals in gray matrix. No eutectic structure.

17. $NiNO_3$-$AgNO_3$. Long green acicular crystals. Lighter green matrix.

18. $CdCl_2$-NH_4Cl. Type M diagram. Eutectic 56% ammonium chloride. 267°C. Figure 2-d. Very fine sliver-like white crystals of ammonium chloride in darker $CdCl_2$. Compound formed (see diagram).

19. $CdCl_2$-NaCl. Type R diagram. Eutectic 45% NaCl, 392°C. Small polyhedral crystals.

20. $CdCl_2$-$CoCl_2$. Lamellar eutectic. Figure 2-g.

21. $K_2Cr_2O_7$-KBr. Figure 2-c. Orange crystals of potassium dichromate in a yellow matrix (probably a compound).

22. $CoCl_2$-KCl. Blue primary crystals in green and blue eutectic matrix.

23. $CoCl_2$-$PbCl_2$. Large white crystals of primary lead chloride in salt-and-pepper-like eutectic.

24. $CuSO_4$-$FeSO_4$. Solidified in two layers with copper sulphate on the bottom.

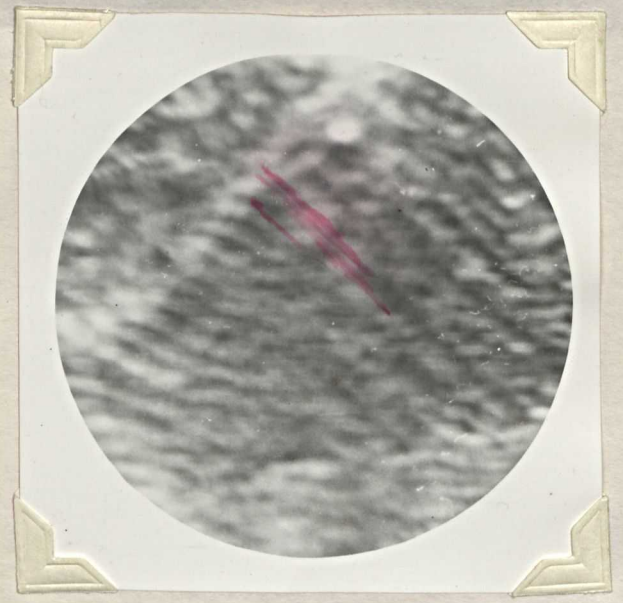
25. $K_2Cr_2O_7$-KCl. Type V diagram. Eutectic 72% potassium dichromate, 366° C. Lamellar eutectic. Orange crystals of potassium dichromate in a yellow matrix (probably a compound). See Figure 2-b. Grain colors differ due to orientation of grains.

26. K_2CrO_4-KNO_3. Type V diagram. Eutectic 2% potassium chromate, 295° C. See diagram. Polyhedral eutectic, small, almost equi-sized crystals of white potassium nitrate in orange potassium chromate.

27. $CdCl_2$-KCl. Type M-R diagram. See Figures 2-f and 6. Small rhombic crystals.

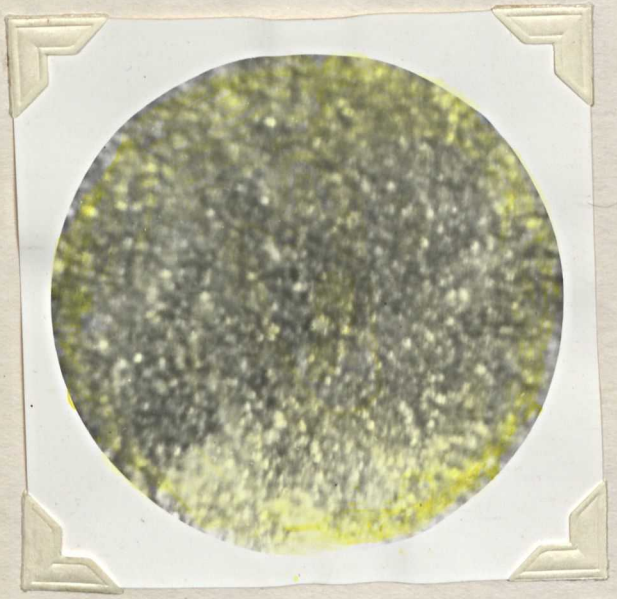
28. $CdCl_2$-$MgCl_2$. Type I diagram. No eutectic formed. Deliquescent nature of magnesium chloride prevented examination.

29. $CuCl_2$-NH_4Cl. Eutectic at approximately 70% ammonium chloride. Ammonium chloride sublimes at 340° C. Polyhedral eutectic. Brown crystals of $CuCl_2$ in white ammonium chloride. Figure 2-h.



a.

b.



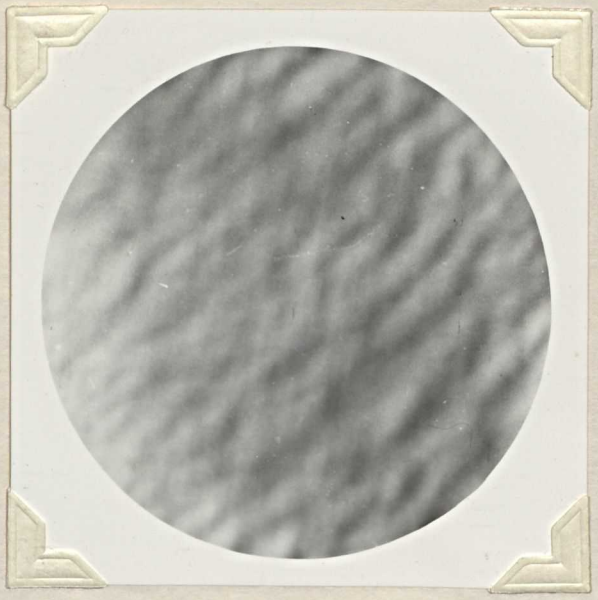
c.

d.

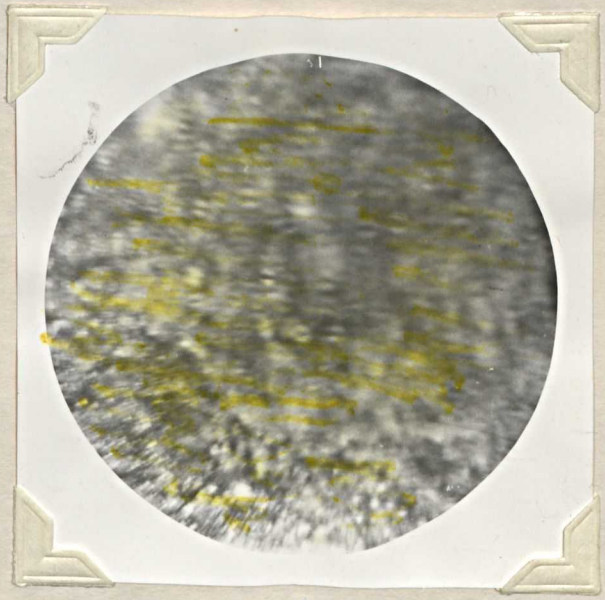
e.

f.

Fig. 2.



g.



h.

Fig 2.

Cu Cl + NH_4Cl.

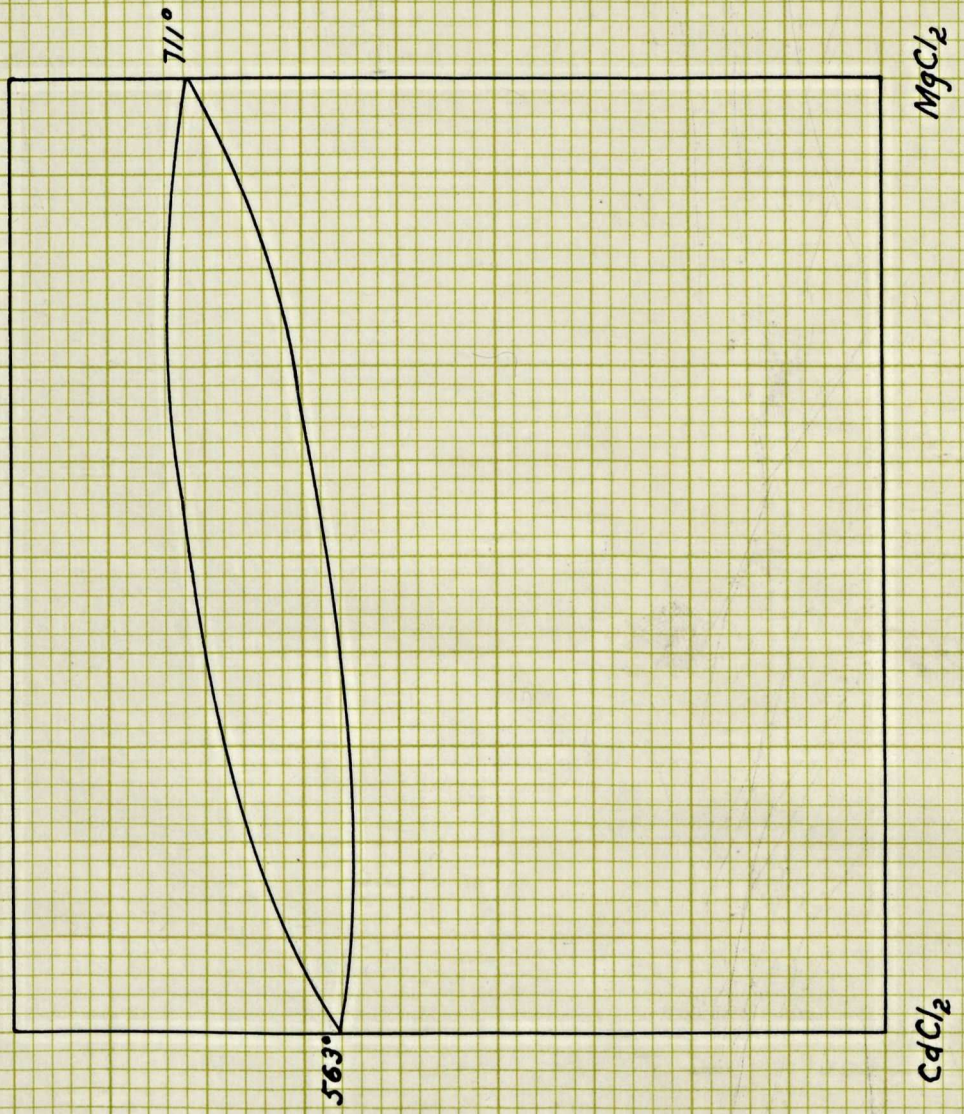


FIG. 3

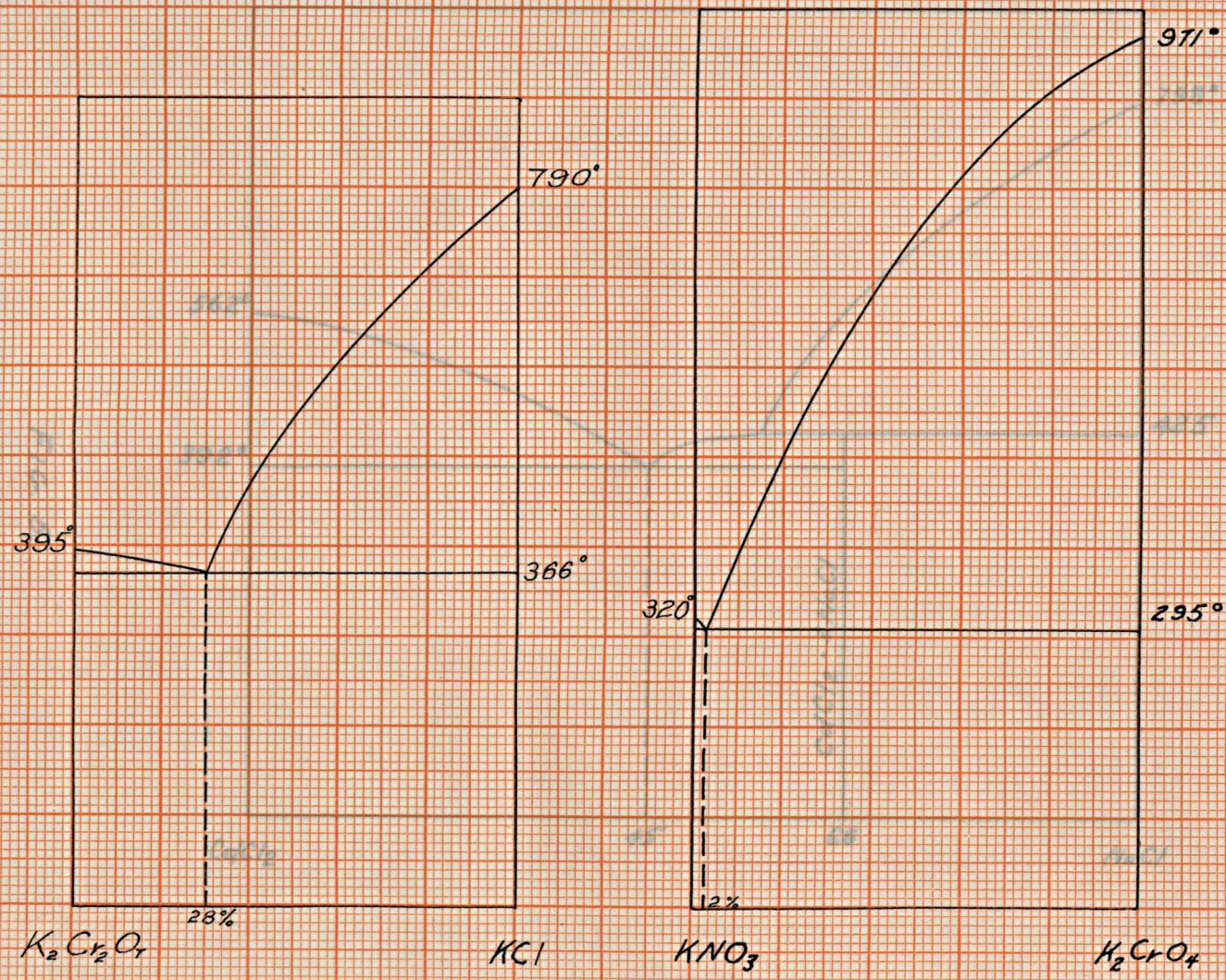


FIG. 4.

(769)

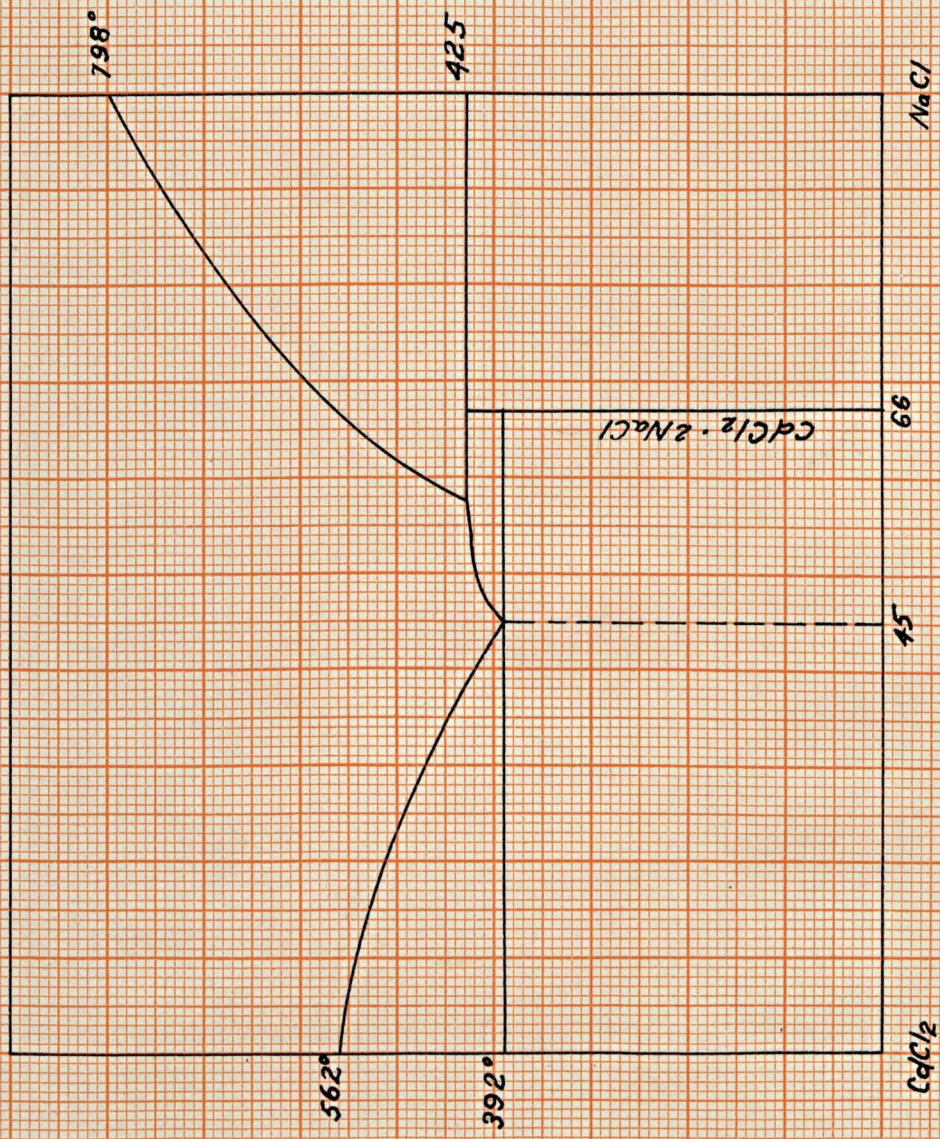


FIG. 5.

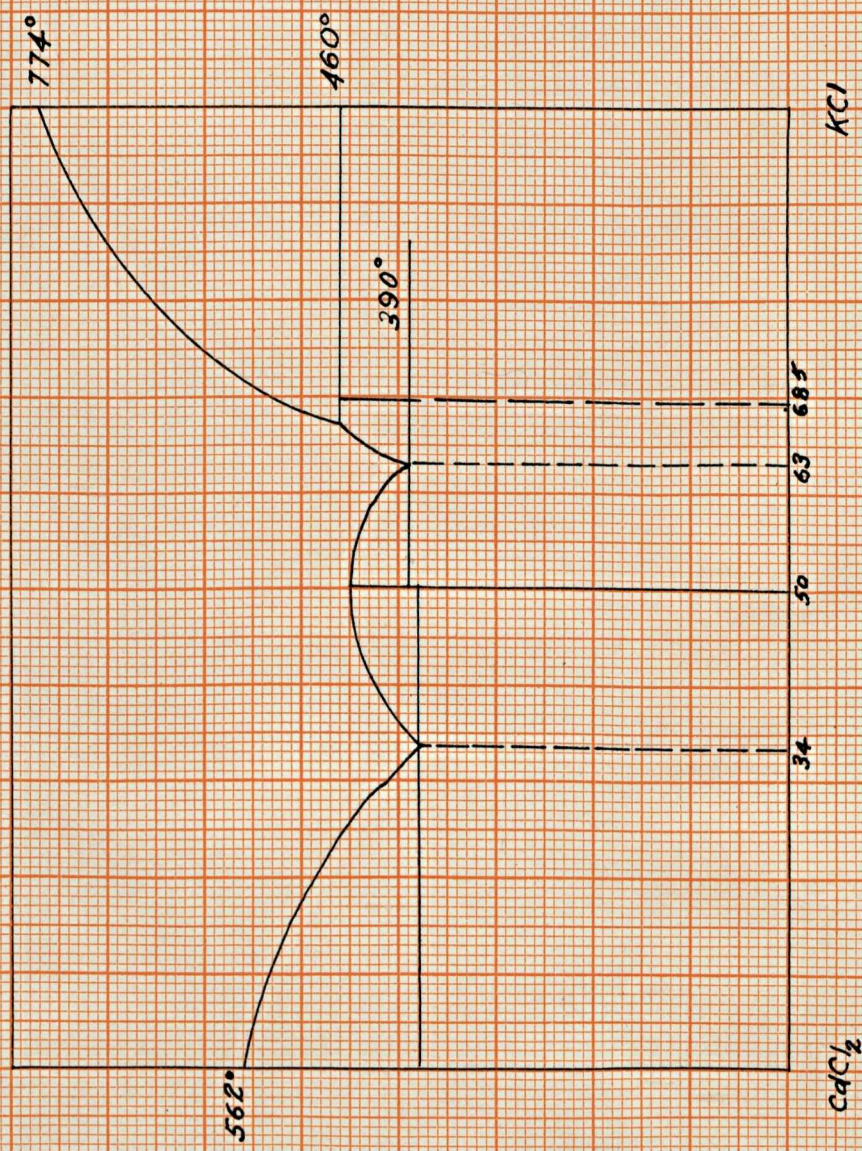


FIG. 6.

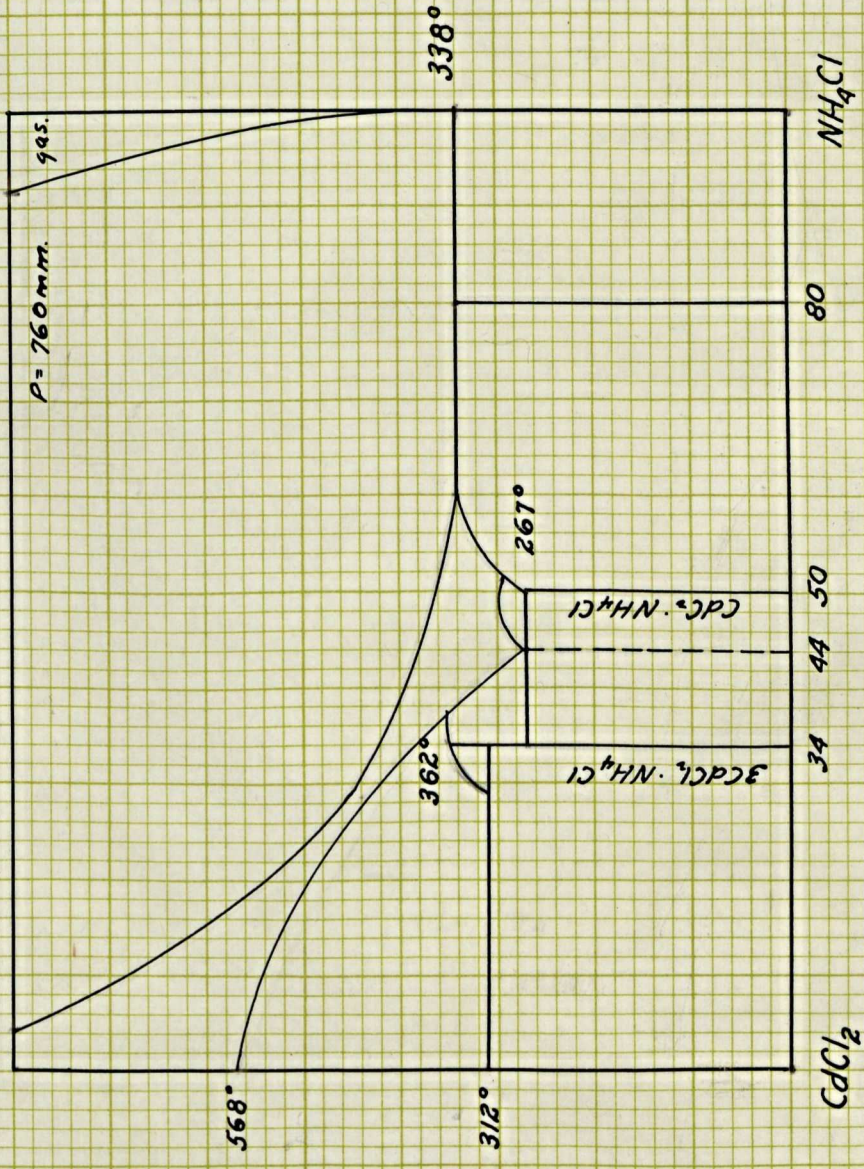

338°
NH_4Cl
945.
P = 760mm.
80
267°
$CdCl_2 \cdot NH_4Cl$
50
44
34
362°
$3CdCl_2 \cdot NH_4Cl$
568°
312°
$CdCl_2$

FIG. 7.

Conclusion

Although the author can report no startling discoveries from his work, he feels that it has been successful in that it has taught him the principles involved and he hopes that the experimental technique here worked out may be of some value, however small, to subsequent experimentors.

The thrill of working on a problem independent of others, the collecting and reading of available books and periodicals on the melting and preparation of specimens, and lastly the taking and printing of microphotographs well repayed the small amount of time spent.

Acknowledgment

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BIBLIOGRAPHY

[1] Landolt Bornstein (Diagrams)

Chemical Abstracts

6:703, 8:2659, 8:1714, 7:11, 17:3270

17:49, 18:3301, 22:2501, 28:1594, 25:326.

International Critical Tables (Diagrams)

Mellor--A Comprehensive Treatise on Inorganic and Theoretical Chemistry.

The Encyclopaedia Brittanica